

ARMY RESEARCH LABORATORY



# Reduced Volatile Organic Compound (VOC) Ammunition Coatings

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## TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION .....	1
2. METHOD .....	2
2.1 Pigment System .....	2
2.2 Binder System .....	3
3. RESULTS .....	3
3.1 Pigment System .....	4
3.2 Binder System .....	5
4. DISCUSSION .....	5
DISTRIBUTION LIST .....	7

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## LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Pigmentation .....	2
2.	Test Requirements .....	4
3.	Pigmentation Without Lead Chromate .....	4

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## 1. INTRODUCTION

Protective coatings for Army ammunition must meet production requirements not found when painting tactical equipment. First, regardless of the size of the projectile, there is a definite limit on the dry film thickness, usually about 1.5 mil (1 mil = 0.001 in), because the round must fit into the weapon's chamber. Second, since ammunition production rates are typically very high, especially when compared to those of tactical equipment, the dry/cure time must be very short. Ammunition is often shipped within 24 hr of manufacture, and the paint must be sufficiently cured to provide acceptable protection, such as corrosion resistance, and not stick to any container or packaging materials. To assist in the drying process, most ammunition plants require a half-hour force cure in an oven at approximately 250° F. The predominant substrate is steel with a zinc phosphate pretreatment.

Due to the drying-time limitation, systems which cure by cross-linking (e.g., by oxidation as in an air-drying alkyd or by catalysis as in a two-component epoxy) are not used. In addition, the dry film thickness limitation generally requires that ammunition coating systems consist of a single film. Therefore, this single film must provide the corrosion resistance of a primer, plus such properties as color, gloss, and solvent resistance that are required of a topcoat. This is a compromise, at best. Historically, the solution to these requirements has been the combination of chromate-containing pigments for corrosion resistance with lacquers (or fast-drying enamels) as the binder for rapid drying. Neither the pigmentation nor the binder would be acceptable by today's environmental standards.

For example, federal and local regulations resulting from the Clean Air Act and its amendments restrict the amount of volatile organic compounds (VOCs) emitted during the application of protective coatings, and Occupational Safety and Health Administration (OSHA) regulations on worker safety restrict exposure to many of the materials used in their manufacture. These materials also generate hazardous wastes and the associated high disposal costs. This effort is designed to pursue the development of ammunition coatings that perform as well as or better than current systems, while solving the regulatory problems previously mentioned. For large-caliber ammunition, the workhorse document is MIL-E-52891, Enamel, Lusterless, Zinc Phosphate, Styrenated Alkyd Type. In its current state, it has a VOC of about 600 g/l as applied, and it allows the use of lead chromate in three of the colors at up to 24% by weight of the pigment.

In this first year for the program, the objective was to survey a sampling of the available high-solid (HS), water-reducible (WR), and waterborne (WB) binder technologies in both air-dry and baking-type systems that had the potential for providing the desired improved performance and corrosion resistance at reduced VOC levels. The main preliminary screening requirement was rapid air drying or, alternatively, successful force curing during the usual ammo plant bake cycle of 250° F for a half hour. In addition, pigment systems free of lead or hexavalent chromium (chromate) would be incorporated.

## 2. METHOD

2.1 Pigment System. Over the past 10 or 15 yr, this laboratory has developed pigment systems free of lead and chromate for a variety of camouflage colors in protective coatings used on tactical equipment. Since the Army rarely changes color requirements (the major exception to this generalization being the switch for tactical equipment from four-color to three-color patterns with new colors in the mid-1980s), the problem colors in MIL-E-52891 are colors that have previously been reformulated to environmentally acceptable standards. As can be seen in Table 1, which summarizes the pigment requirements from MIL-E-52891, the colors forest green, olive drab, and light green all require or allow the use of medium chrome yellow pigment, which is lead chromate. Reformulation without the use of medium chrome yellow is the desired goal for these colors.

Table 1. Pigmentation

Color, Color No. in FED-STD-595	Percent by Weight Prime Pigment (min.)	Prime Pigment	Pigments Allowed
Forest green, No. 34083	20	Fe <sub>2</sub> O <sub>3</sub>	yellow iron oxide, medium chrome yellow, phthalocyanine (phthalo) blue, carbon black
Olive drab, No. 34088	24	Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	yellow iron oxide, medium chrome yellow, titanium dioxide, carbon black, red iron oxide
Light green, No. 34558	36	TiO <sub>2</sub>	yellow iron oxide, medium chrome yellow, titanium dioxide, carbon black, phthalo blue or green

<sup>a</sup>Lead chromate (PbCrO<sub>4</sub>) may be substituted on an equal weight basis.

2.2 Binder System. Over the past few years and before this work was initiated, commercial products have been solicited and evaluated as environmentally acceptable substitutes for MIL-E-52891 where local VOC regulations so dictated. They can be divided into three broad categories: (1) coatings for ammunition containers, (2) standard coatings for ammunition, and (3) high-performance coatings for large-caliber ammunition. Typically, alternate ammunition container coatings have been baking-type alkyds, standard coatings have been either WR or HS alkyds, and high-performance coatings have been force-cured epoxies or polyurethanes. The future for ammunition coatings is unclear at this point because of the chemical agent resistant coating (CARC) factor. With one major exception, to be discussed later, ammunition and ammunition containers have not had a requirement for chemical agent resistance. If that policy continues, then the reformulation of MIL-E-52891 will be a "low-tech" solution of a WB, WR, or HS alkyd similar in performance to MIL-E-11195, Enamel, Lusterless, Fast Dry, VOC Compliant. This material, which was reformulated in this laboratory for VOC compliance, has been used primarily on small-caliber ammunition.

As part of a cooperative effort with the U.S. Army Armament Research, Development, and Engineering Center (ARDEC) to improve the corrosion resistance of large-caliber projectiles, coatings in the CARC system have shown potential in two areas. First, the M864 projectile coating requirement consists of the standard CARC primer MIL-E-53022, Primer, Epoxy Coating, Corrosion Inhibiting, Lead and Chromate Free, followed by a topcoat of MIL-E-52891 for color/identification. However, the limit on film thickness for this projectile is 2.0 mil vs. the normal 1.5 mil, and this essentially allows for more paint to provide more protection. The second use of CARC is on the Sense and Destroy Armor Munition (SADARM). This is a new, "smart" projectile that had a chemical agent resistance requirement from the beginning. With only 1.5 mil as the upper limit on film thickness, a single coating would need to provide both chemical agent resistance and corrosion resistance.

### 3. RESULTS

As noted earlier, the primary requirement of an ammunition coating is that it dries fast. That, combined with the strict upper limit on film thickness, has resulted in coating systems with less-than-ideal corrosion resistance. Along with the lower VOC limits likely in the future come potential complications, such as poorer performance with WR/WB coatings and difficulty in meeting film thickness requirements with HS coatings. Performance of materials evaluated so far has been compared to a selection of tests from MIL-E-52891 as shown in Table 2. The VOC limitation has been  $\leq 3.5$  lb/gal.

Table 2. Test Requirements

Test	Requirement in MIL-E-52891
Color	Visual match to FED-STD-595 chip
Specular gloss	8 maximum
Water resistance	18-hr immersion
Salt spray (fog) resistance	150 hr (scored)
Accelerated weathering	240 hr in Xenon arc weatherometer

3.1 Pigment System. The solution to the lead chromate problem for camouflage coatings has been to substitute a zinc or magnesium ferrite pigment. An example of such a pigment would be Mapico Tan 20 from Columbian Chemical. However, since ammunition coatings simply identify the type of round and do not have the infrared reflectance requirements typical of camouflage coatings, good visual matches without lead chromate would use a simple yellow iron oxide substitution along with an adjustment to the other pigments in the mixture. Zinc phosphate is in the formula at about 15% of the dry pigment weight as the chromate-free anticorrosive pigment. Therefore, good working formulations for the noncamouflage forest green and olive drab colors would be as shown in Table 3. These formulae are simple, economical, and durable.

Table 3. Pigmentation Without Lead Chromate

Pigment	Percent by Weight of Pigment	
	Forest Green	Olive Drab
Yellow iron oxide	19.5	28.2
Titanium dioxide	10.2	5.2
Carbon black	3.2	1.1
Phthalocyanine blue	2.1	—
Red iron oxide	—	0.5
Zinc phosphate	15.0	15.0
Extenders	50.0	50.0

3.2 Binder System. Because of the availability of ovens at the manufacturing sites, the alternate coatings for ammunition containers have been melamine-modified, thermally cured, alkyd enamels. This is a much better binder than the MIL-E-52891 air-drying system, so performance is much better. But strictly speaking, however, these are not production-compatible ammunition coatings because of the required bake vs. a lower temperature force cure typical of ammo plant capability (i.e., 10–15 min at 350° F vs. 30 min at 250° F). The air-drying WB coatings evaluated to this point as standard ammunition coatings have had deficiencies, usually in the corrosion resistance. The HS option reduces, essentially, to an improvement in the corrosion resistance of MIL-E-11195, probably via the addition of zinc phosphate anticorrosive pigment to the system. The CARC-type systems have performed very well. While the M864 long-term corrosion and color-stability testing is still underway, preliminary results are good. However, this system is unique in its 2.0-mil dry film thickness allowance. Similarly, very early test results from this laboratory on the single-coat, moisture-cure polyurethane now specified for the SADARM are also very good. The material is VOC compliant, chemical agent resistant, and provides improved corrosion resistance over MIL-E-52891. However, the corrosion resistance may need further improvement to provide the protection necessary for such an expensive projectile, particularly since most production rounds will be subject to long-term storage.

#### 4. DISCUSSION

At this point, it seems that it will be very difficult to reconcile the varying needs of the container, ammunition, and SADARM-type protective coating requirements into one specification, and divergence may be inevitable. A single HS/WB coating should suffice for small-caliber ammunition, ammunition containers, and large-caliber projectiles without the need for CARC, because the performance and production requirements are compatible (i.e., fast air dry or force cure along with acceptable performance). However, the single-coat polyurethane will be used increasingly on large munitions due to the imposition of CARC requirements, and possibly on some ammunition containers. Plans for the future include:

- a. Obtain a list of users through the General Services Administration and/or ARDEC and survey their equipment capability and environmental restrictions.
- b. Continue the dual-track efforts in formulation (i.e., the high-quality CARC systems for large, expensive munitions, and the normal HS/WB systems for standard applications).

c. Investigate the potential for commercial powder coatings to be used for improved corrosion resistance and excellent environmental benefits.

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